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PROSPECTIVE SYSTEMS FOR LASER SEPARATION OF DEUTERIUM

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Prospective Systems for Laser Separation of Deuterium*

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Abstract

Bimolecular 4- and 6-center addition reactions into unsaturated hydrocarbons may be optically accelerated with 3-6 quanta provided by CO laser excitation of DBr or DCl or by DF laser excitation of HDO or DF. Unimolecular decomposition of HDCO occurs with high selectivity by a single uv photon. Multi-quantum CO₂ laser excitation can lead to 4-center molecular elimination from deuterated organic alcohols and acids.

Bimolecular Addition Reactions

Several potentially interesting systems exist for deuterium separation by laser catalysed bimolecular addition reactions. Deuterium halide or water, HDO, addition into simple olefins occurs by a homogeneous 4-center reaction and addition into conjugated olefins occurs by homogeneous 4- or 6-center reactions. These systems are interesting, since these homogeneous reactions occur in the gas phase and are not affected by surface reactions. Also, the unsaturated hydrocarbon may be chosen to yield a sufficiently low activation energy that 3-6 quanta of DX or DO stretch excitation may be sufficient for acceptable reaction quantum efficiencies. These systems may be excited by the efficient and high average power CO or DF lasers according to the reactions:

- (1) $\text{DBr} + n h\nu \text{ (CO laser)} + \text{olefin} \rightarrow \text{brominated alkane-d}_1$
- (2) $\text{DCl} + n h\nu \text{ (CO laser)} + \text{olefin} \rightarrow \text{chlorinated alkane-d}_1$
- (3) $\text{DF} + n h\nu \text{ (DF laser)} + \text{olefin} \rightarrow \text{fluorinated alkane-d}_1$
- (4) $\text{HDO} + n h\nu \text{ (DF laser)} + \text{olefin} \rightarrow \text{alcohol-d}_1$

The known or calculated Arrhenius parameters for these reactions are given in Table I. The pre-exponential or A factor is generally independent of reactant for a given olefin.

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TABLE I¹
Arrhenius Parameters for $\text{HX} + \text{Olefin} \rightarrow \text{Product}$; $\text{X} = \text{Br}, \text{Cl}, \text{F}, \text{OH}$

Olefin	Pre-exponential ^a $\log_{10} A$	Activation Energy, E_a (kcal/mole)			
		H_2O	HF	HCl	HBr
Ethylene	8.3	57	50	40	34
Propylene	7.9	52	45	34	29
Isobutene	6.3	49	41.5	26	23
1,3-butadiene	8.8	47*	40*	28*	24*
1,3-pentadiene	7.7	42*	35*	24*	20*
Phenylethylene	~ 8.0	47*	39*	31	22
4-methy-1,3-pentadiene	6.5	39*	32*	19*	15*

^a A units are liter/mole sec.

* Estimated Values, E_a accurate to ± 3 kcal/mole.

Table I shows that activation energies may be chosen as low as 20-30 kcal/mole, and that conjugated olefins are the best reactant choices. Details of spectroscopy for DCl and DBr for CO laser excitation are discussed in UCID-16999². Each system offers significant advantages and disadvantages summarized below, rendering an *a priori* choice difficult.

- H_2O - Permits greatly simplified process engineering
 - Permits use of DF laser excitation
 - Has highest reaction activation energy, twice as high as HBr
 - Experiences rapid vibrational self-deactivation
- HF - Toxic corrosive material
 - "Automatic" match to DF laser excitation, 100% efficient absorption
 - Intermediate activation energies and vibrational deactivation
- HCl - Common but corrosive industrial material
 - Permits excitation by efficient well developed CO laser technology
 - Absorption strength is 5 times stronger than HBr
- HBr - Also has convenient match to CO laser excitation
 - Has lowest activation energy of all practical reactants
 - Has greatest resistance to vibrational deactivation
 - Absorption bands 5 times weaker than HCl

Unimolecular Reactions

Formaldehyde has a well established photochemistry leading to highly selective enrichment of deuterium, following single quantum near ultra-violet excitation³. The reaction would proceed as follows:

The photochemistry is nearly ideal, since the quantum efficiency is nearly 100%, and the decomposition products are the stable hydrogen and carbon monoxide molecules. Isotope scrambling can be made less than 10%⁴. Single step enrichment factors of order 100-fold are demonstrated^{3,4}, and dozens of untested lines may permit enrichment of order 1000-fold to be achieved. The disadvantages are the difficulty of achieving liquid or vapor phase deuterium exchange with water for replenishing the feedstock. Also required is uv laser efficiency of order 1%. Perhaps the largest limitation is the requirement of a fraction of a megawatt of average uv laser power in an average-sized (500 tons D₂O/year) plant. However, it certainly has an excellent photochemistry and is presently the only proven laser-driven deuterium isotope separation process with acceptable photon utilization.

Multiphoton dissociation of suitable molecules using the well established CO₂ laser technology naturally must be carefully considered. Absorption of 50-100 quanta has been required to blow apart molecules such as SF₆ and even H₂CO with high isotopic selectivity. For deuterium separation we may take advantage of 4- and 6-center homogeneous elimination reactions to greatly reduce the energy barrier to dissociation. An example of a potentially interesting system is dissociation of t-butyl bromide:

The Arrhenius factors are⁵: $A = 6 \times 10^{13} \text{sec}^{-1}$, $E_a = 41.8 \text{ kcal/mole}$

Thus, such a system has a reasonably low activation energy, produces stable molecular products, and has an extremely high pre-exponential, or frequency factor compared to the bi-molecular addition reactions discussed earlier. Furthermore, it has 9 identical H-atoms that can carry deuterium, increasing thruout 9-fold. However, it is not clear how to tie it to an aqueous exchange to replenish the deuterium, which is its only major disadvantage.

Organic molecules which do easily exchange a proton in aqueous solutions are the alcohols and organic acids. Fortunately, homogenous molecular elimination reactions occur for these, and furthermore, activation energies can be as low as ~30 kcal/mole, or 2-3 times lower than the minimum energy to dissociate molecules into radicals. Several interesting reactions are listed. The alcohol analogue of reaction (6) is t-butyl alcohol $\rightarrow$ H₂O + isobutene which has 20 kcal/mole higher activation energy⁵. The following reactions may be more interesting due to their low activation energies⁵ (reaction rates are given as $k = A(\text{sec}^{-1}) e^{-E_a(\text{kcal/mole})/RT}$):

Alcohols

$$k = 6 \times 10^{11} e^{-39/RT}$$

$$k = 2.5 \times 10^{13} e^{-61.6/RT}$$

Acids

$$k = 2 \times 10^{11} e^{-40.6/RT}$$

$$k = 7 \times 10^{10} e^{-32.3/RT}$$

$$k = 8 \times 10^{11} e^{-30/RT}$$

Reactions (7) - (9) involving alcohols may be less attractive due to strong absorption bands at CO₂ laser wavelengths in the normal (undeuterated) species⁶. Reaction (6) is interesting since t-butyl chloride or t-butyl bromide are very transparent from 9-11 microns, and strongly absorbing for the mono-deuterated species⁷. This process is being evaluated at U.S.C.⁷. Reactions (10) - (13) are interesting because of the low activation energies and because these molecules are transparent⁶ in the 1040 cm⁻¹ region accessible by 9.6 micron CO₂ lasers, with absorption expected for the deuterated species.

In bimolecular reactions the gaseous reaction rate is proportional to the product of the Arrhenius A coefficient and the olefin concentration. This factor will typically be about 5 $\times$ 10⁶ sec⁻¹ for reactants at 1 atmosphere pressure. In comparison, the pre-exponential factor for unimolecular 4-center elimination reactions is about 10⁵-10⁷ times higher, which compensates for activation energies 10-20 kcal/mole higher than for bimolecular addition reactions, and permits reaction rate to more easily beat quenching.

This summary of prospective systems for laser separation of deuterium is not intended to be comprehensive, but simply to point out the several interesting possibilities. Intensive experimental evaluation will be required to select the system most suitable for realistic industrial application for laser production of heavy water. All systems mentioned will certainly permit extensive evaluation of laser-induced chemistry.

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